

The Molecular Basis for the Heat Capacity and Thermal Expansion of Natural Waters

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Abstract

The high heat capacity (C_p) of water drives absorption by the ocean of 93% of the heat trapped by anthropogenic greenhouse gases. Specific heats are closely tied to molecular weight. Here we show that the mean molecular weight of water over the range 0-40°C is 86.1-80.7. Warming of water increases the translational energy of the molecules, and induces breaking of hydrogen bonds (8.364 kJ/mol) both increasing the volume of the fluid. Warming sea water by 10°C increases the single H₂O molecular form by 1.64%, accounting for 36% of the energy consumed. The heat capacity of water is attributable (64%) to the mass of the hydrogen bonded forms, and (36%) to the energy required to break hydrogen bonds. C_p for water decreases with temperature with the decrease in molecular weight; C_p for sea water increases due to the work required to increase the translational energy of the large hydrated cations.

Introduction

The molecular basis for trapping of heat within the atmosphere by the CO₂ molecule and related greenhouse gases has long been known, and it provides the foundation underlying all studies of modern climate change and greenhouse gas driven global warming. But the molecular basis and consequences for the large scale opposing process – the remarkable absorption by the ocean of some 93% of the heat trapped by anthropogenic greenhouse gases (Rhein et al., 2013; Cheng et al., 2017) – is poorly understood. This seems unwise given the importance of the process in the planetary heat balance. The effect is usually attributed to the large size of the ocean, the omnipresent stirring by wind, and the “high heat capacity” of water and sea water. What is meant by high heat capacity (C_p) is typically stated simply within the Earth science literature as a bulk specific heat property without further inquiry. In marked contrast the molecular basis for the absorption by the ocean of some 25% of industrial CO₂ emissions via the reaction with carbonate ion and the resulting reduction of pH is now well known (Brewer, 1997; Gattuso and Hansson, 2011). Yet there is a substantial, albeit confusing, literature on the molecular basis for the absorption of heat as a property of water. The absorption of heat also increases the specific volume of the fluid and this phenomenon is closely tied to molecular properties governing C_p . The purpose of this paper is to introduce the topic as applicable to natural waters, and to begin to quantify where possible the processes underlying this remarkable phenomenon without which we would not have a habitable planet.

Various web sites do provide some introductory material noting that the high heat capacity is related to the fact that water is a hydrogen bonded fluid, but typically do not develop the argument beyond that. Water is essentially a bi-molecular fluid with free non-hydrogen bonded (nHB) H₂O molecules in a temperature controlled dynamic equilibrium with a complex of many hydrogen bonded (HB) forms. Sea water is 96.5% water by weight and recent work (Brewer et al., 2018) has shown that it is possible to quantify the water species present so that the amounts of the nHB form, and the ensemble of HB forms, can be precisely determined. The ensemble of

HB forms has no specific identity – it is a labile population of rapidly exchanging forms with local structural heterogeneities where “hydrogen bonding states associated with the formation of four hydrogen bonds by a water molecule exhibit the largest survival probability and corresponding lifetime” (Guardia et al., 2014). The heat capacity of sea water is dominated by the water terms and the specific heat of pure water is higher than that of sea water.

There have been efforts to describe the heat capacity of water in molecular terms (Benson and Siebert, 1992) based on a “simple two structure model” of water octamers and tetramers, but this does not seem to correlate with modern Raman spectroscopic measurements (Carey and Korenowski, 1998; Smith et al., 2005; Brewer et al., 2018). There are also efforts to solve the reverse problem – to deduce the molecular structure of liquid water based on the evidence provided by the observed heat capacity (Dougherty and Howard, 1998); the topics are tightly coupled.

Here we use recent Raman spectroscopic data to provide a first-order description of the molecular processes involved when greenhouse gas generated heat is transferred to ocean waters. It will not be possible to solve the problem exactly but the lack of papers discussing this subject matter in the oceanographic literature suggests that a simple description here will be useful.

Analysis

The first question we might ask is why the heat capacity of water is so large, second only to liquid ammonia. A general theory of the heat capacity of liquids has not yet been achieved. On a per atom basis all substances have a heat capacity close to the Dulong-Petit limit (Petit and Dulong, 1819) of $3R$ per mole of atoms where R is the universal gas constant. On a per mole basis heat capacity is strongly correlated with molecular weight – it takes more work to increase the translational energy of a large (heavy) molecular structure than a smaller (lighter) one and for water the molecular size distribution has no single or unique value. Within the water population family of HB and nHB species, molecular size and weight are strongly correlated.

The effect of heating a fluid is first to increase the translational energy of the molecules – immediately raising the question of which molecules are present. And in the case of water we must also consider the energy taken to break hydrogen bonds. Observations show that on warming of water and sea water the population of nHB molecules increases, and the ensemble of HB forms decreases (Walrafen, 1964, 1967; Brewer et al., 2017, 2018). The breaking of hydrogen bonds is the inescapable result of this process.

The strength of the hydrogen bond has been reliably estimated (Silverstein et al., 2000; Smith et al., 2005) as 2 kcal/mol (8.364 kJ/mol). Thus in order to describe ocean warming in molecular terms we need to determine the abundance of the various molecules present at any temperature, and how many bonds are broken for a specific temperature change. This is no easy task.

i) *The ensemble molecular weight of water*

Water has no fixed or easily determinable molecular weight. The formula weight for water is typically given as 18. But the single nHB H_2O molecules represent only a small fraction of the liquid population, and that fraction is temperature dependent. The dominant HB species is the Walrafen tetrahedral pentamer, with a molecular weight of 90, but this exists within a sea of

other molecules of both lower (trimer, tetramer), and higher (hexamer, heptamer, etc.), molecular weights.

There is no agreement on the ensemble value for this fluid although, taking stable isotope populations into account, it must be discretized in multiples of 18.0153 for the molecular weight of the various n-mers. For simplicity we have assumed the “tall pole” to be the Walfrafen tetrahedral pentamer bounded by a Gaussian-like distribution of the other species. We note also the simultaneous presence of a planar pentamer form, also of molecular weight ~90. The actual distribution of the various n-mers is unknown as Raman spectroscopy can only distinguish between nHB molecules and those within the HB species. However, as long as the molar distribution is symmetrical and centered on the pentamer, the mean molecular weight of the clusters remains the same. One then only needs to know the ratio of nHB H₂O species to the HB species to calculate the ensemble molecular weight (Table 1).

The ubiquitous presence of pentamers and hexamers in ocean water is readily observed in the rapid formation of gas hydrates. These HB ice-like solids hosting gas molecules are found in huge quantities in gas rich sediments and are readily synthesized in the ocean water column, and in sediment pore waters, by simple gas injection (Brewer et al., 1997; Kleinberg et al., 2003; Hester et al., 2007). The structures are based on pentamer and hexamer water species recruited from the liquid state and a common form of the hydrate water cage is the 14 sided tetradecahedron with 12 pentagonal and 2 hexagonal faces (Sloan and Koh, 2008).

In Figure 1A we show a schematic of one possible distribution of water species in pure water at temperatures of 0°C and 40°C. The ensemble molecular weight decreases slightly with rising temperature as the population of large HB forms decreases. From the example shown in Figure 1A, we estimate the ensemble molecular weight of water at 0°C to be 86.1, and at 40°C to be 80.7.

In the case of sea water the presence of salts adds further complexity. The effect of dissolved salts, dominantly the cations, is to recruit a hydration shell of typically 6 individual water molecules arranged around the ion. These molecules are recruited from the bulk fluid and diminish the population of all HB forms and the free nHB form proportionally (Brewer et al., 2018). The molecules in the hydration shell are not hydrogen bonded, nor are they free. They are held in place by a dative covalent bond – some 20x stronger than the hydrogen bond – and the quantity appears to be independent of temperature and pressure. The matter of possible anion effects on the HB structures is far less certain, but the presence of anions does tend to affect the ordering of neighbor water molecules (Hribar et al., 2002).

The molecular weight of the salts contributes to the overall mass; but only the sulfate ion (SO₄²⁻), with a molecular weight of 96, exceeds that of the water pentamer. The water component in the hydration shell must be added to the weight of the cation since the two are inseparable in aqueous solution – thus a sodium ion of mass 23 with its 6 water molecule hydration shell will have a formula mass of 131. From the example shown in Figure 1B, we estimate the ensemble molecular weight of sea water ($S_p = 35$) at 0°C to be 89.4, and at 40°C to be 84.5 (See Table 1).

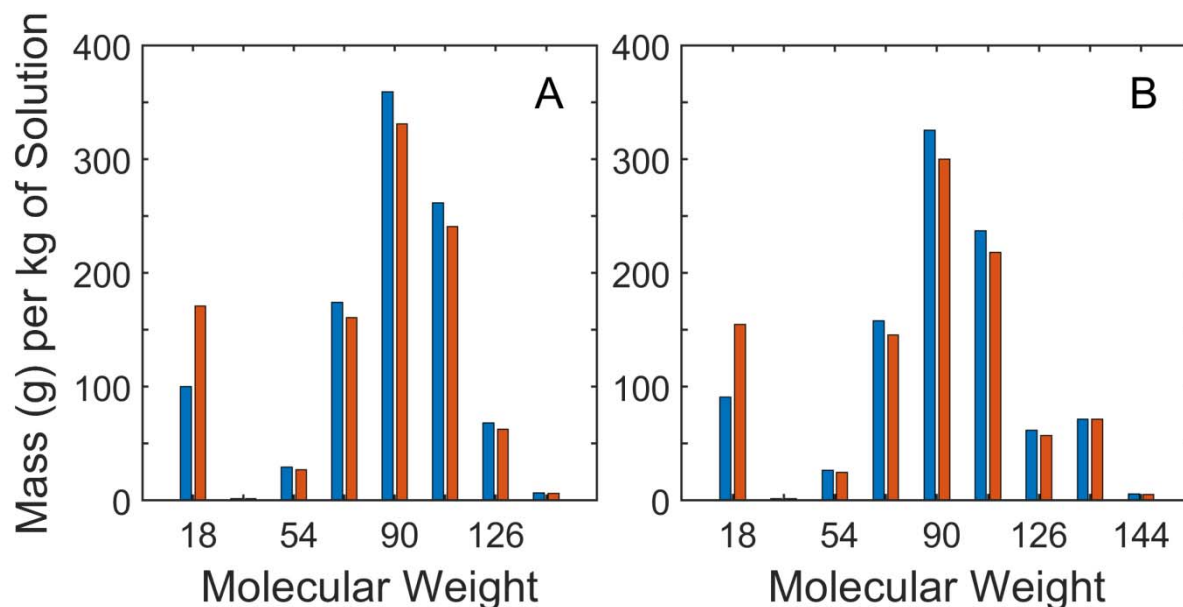


Figure 1. (A) Schematic of one possible distribution of molecular weights of water species in pure water at temperatures of 0°C (blue bars) and 40°C (red bars) assuming that the pentamer forms are dominant and the other HB forms have a Gaussian distribution around the pentamer. **(B)** Schematic of one possible distribution of the water species in sea water ($S_p = 35$) at temperatures of 0°C and 40°C, assuming that pentamer forms are dominant, and that the other water species have a Gaussian distribution around this point (see text). The additional pair of bars between molecular weights 126 & 144 are the mass of the cations with water solvation spheres and an ensemble molecular weight of 131.85. The cation concentrations do not vary with temperature.

ii) Specific heats

The specific heats of water and sea water of various salinities at constant pressure (C_p) are well known. For a convenient example we use here the compact and accurate data of Cox and Smith (1959). In Figure 2 we replot their data for pure water, and for sea water, as a function of temperature.

The data shown in Figure 2 show two clear effects that require explanation: 1) the specific heat of pure water is higher than that of sea water, and 2) the trends with temperature are reversed; the specific heat of pure water decreases with rising temperature as the population of the single H_2O form increases thus reducing the average molecular weight, yet the specific heat of sea water increases with rising temperature.

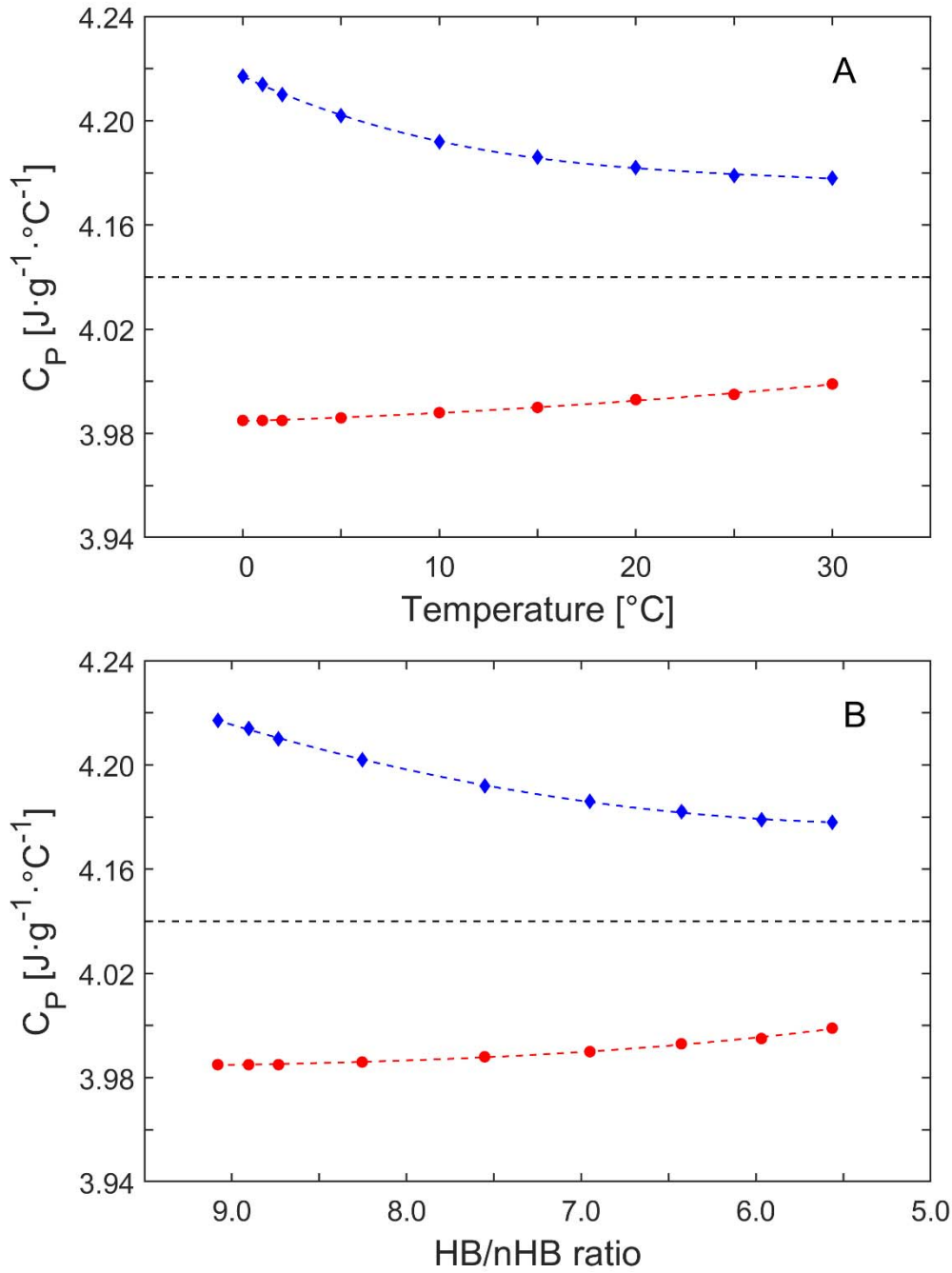


Figure 2. Specific Heats (C_p , Cox and Smith, 1959) for pure water (blue diamonds) and sea water ($S_p = 35$, red dots) as a function of Temperature **(A)** and the molar ratio of HB to nHB water molecules **(B)**. Pure water has a higher C_p which decreases as temperature rises while sea water has a smaller C_p that increases with increasing temperature.

The overall reduction in C_p for sea water versus pure water can be attributed to the recruitment of water molecules primarily from the high molecular weight HB pool into the hydration shells of cations (Brewer et al., 2018) where it is present in single molecular form. The anion contributions to changing water structures are less well known, but they plainly represent a “local structural heterogeneity” by which the tendency of the water molecules to form large temporary structures is disrupted. Overall there are simply fewer HB pentamers in a kg of sea water than in a kg of pure water and this accounts for a large fraction of the reduced heat capacity of salt waters. Beyond this the sea water trend towards increasing C_p with rising temperature requires further explanation.

These data reveal the competing effects of two simultaneous processes: the ensemble molecular weight of water in sea water must decrease (and the specific volume increase) with rising temperature just as for pure water for in both cases the population of nHB forms increases. But this effect is more than compensated for by the increasing energy required to thermally excite the water molecules in the cation solvation shell. In place these molecules possess vibrational energy but not translational energy independent of their associated cation – they must move together as a heavy unit. The dative covalent bond makes it increasingly difficult for the hydrated cations to achieve the mean translational velocity of the water molecules in the bulk fluid.

Calculation

From the background information given above it is possible to make some estimates of the relative importance of the two major components that account for the unusually high heat capacity of water and sea water. We need make no judgement as to which HB forms are disrupted by warming – the entire population is shifted. Walrafen (1964) noted that “two hydrogen bonds are broken when one H_2O molecule is liberated in the complete break-down of a tetrahedral network” but such an assumption is not needed here. We can simply take the observed quantity of single H_2O molecules formed and the enthalpy of the hydrogen bond. Spectroscopic observations show that warming of water produces this effect and the molar quantities can now be calculated (Brewer et al, 2018).

i) *Pure water*

Fresh water presents the simplest case and it is now possible to provide a first order estimate of the changes forced by the uptake of heat. The formal concentration of water in water is 55.5084 molar and at the freezing point we have 90% of the molecular species in HB forms, and 10% as single H_2O molecules (Walrafen, 1964).

It takes 42.042 kJ to heat 1 kg of water from 0°C to 10°C. Taking data from Brewer et al. (2018) Table 2, we find that the population of HB forms is reduced to 88.36%. We have liberated 0.913 moles of single H_2O molecules. This can be accomplished by the input of 15.27 kJ. Thus the fraction of the heat capacity that can be assigned to hydrogen bond breaking is some 36.3% of the total – the remainder is due to the energy required to increase the translational energy of molecules with an average molecular weight of ~ 85.5 .

ii) *Sea water*

For sea water of 35 salinity we find very similar conclusions. It takes 39.86 kJ to heat 1 kg of sea water from 0°C to 10°C. Taking data from Table 1, at 35 salinity, we find that this liberates 0.827 moles of single H₂O molecules which can be accomplished by the input of some 13.83 kJ – less than is required for the same mass of pure water. There is simply a lesser quantity of HB forms in sea water than in pure water. Nonetheless the phenomenon of hydrogen bond breaking on ocean warming accounts for some 34.7% of the total heat absorbed. The bulk of the heat capacity is due to the large molecular weights of the combined population of HB forms and hydrated cations.

The difference is that the HB population is responsive to changing temperature whereas the hydrated cation population is independent of temperature. Thus this component plays an increasing role as the ocean warms, and its greater molecular weight requires more energy.

From the data presented in Figure 2A and Table 1, we can calculate by difference the specific heat of the dissolved salts in one kilogram of sea water ($S_p = 35$):

$$C_p(\text{salts}) = [1000 * C_p(\text{sw}) - 906.236 * C_p(\text{pw})] / (35.179 + 0.54198 * 6 * 18.0153)$$

where 35.179 is the mass of dissolved salts, 0.54198 is the number of moles of dissolved cations, 6 is the solvation number and 18.0153 is the molecular weight of the solvation water molecules. The variation of the C_p of the dissolved salts as a function of temperature is shown in Figure 3.

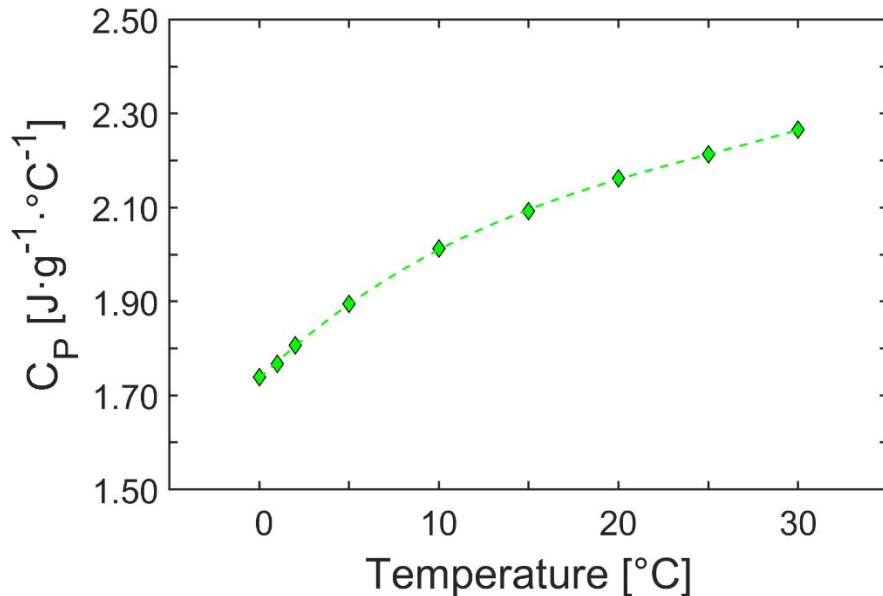


Figure 3. Specific heat of the salts (plus solvation water) dissolved in 1 kg of sea water calculated by the difference between the C_p of pure water and sea water. (See text for the calculation.)

Conclusions

The evidence presented here is further testimony to the huge and under-recognized role of the hydrogen bond in Earth science, for without this water would not be in the liquid state. For heat capacity the bonding plays two roles. Firstly in creating an average molecular weight of water of approximately 83-87 at 20°C, some 4.7 times that of the single molecule; and secondly in the energy required to break apart the dominant HB forms. Although heating of water by 10°C results in an increase of only 1.64% in the population of the nHB form, this accounts for a remarkable 35-36% of the energy input. The increase in specific volume with warming is a direct result of these processes, and while we cannot provide a precise analysis it seems likely that something similar to this ratio holds true for the volumetric changes as well.

In the case of sea water, the recruitment of single water molecules from the ensemble population into the hydration sphere around a cation reduces the population of the large molecular weight HB forms more than the nHB form. This results in the lower heat capacity of sea water compared to pure water within the oceanic temperature range. The retention of water molecules in the hydration shell by the dative covalent bond makes it increasingly difficult for the cation molecular population to achieve the mean translational velocity defined by rising temperature when the scaling factor is provided by $1/T$ where T is in Kelvins.

While the ocean absorbs some 25% of fossil fuel CO₂ emissions, in doing so carbonate ion is consumed and this observably reduces the buffer capacity as ocean pH decreases. In contrast the ocean absorbs some 93% of all anthropogenic greenhouse gas trapped heat – and for salt water the heat capacity actually increases by a small amount as the ocean warms.

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Table 1.

Calculation of pure water molecular weight				Mass water / kg pw = 1000.00g			
		Temp	0	10	20	30	40
		nHB/HB	0.1111	0.1318	0.1545	0.1793	0.2060
		%-nHB	10.000	11.645	13.384	15.202	17.083
		%-HB	90.000	88.355	86.616	84.798	82.917
N-mer	Wt %	Mol Wt	Mass water × (%-nHB or %-HB) × wt % × mol wt				
1	100.0	18.0153	1801.51	2097.84	2411.16	2738.70	3077.59
2	0.1773	36.0306	57.50	56.45	55.34	54.18	52.98
3	3.2403	54.0459	1576.14	1547.34	1516.88	1485.04	1452.10
4	19.3629	72.0612	12557.84	12328.33	12085.65	11831.97	11569.50
5	39.9050	90.0765	32350.59	31759.33	31134.18	30480.67	29804.50
6	29.0443	108.0918	28255.14	27738.73	27192.72	26621.94	26031.37
7	7.5608	126.1071	8581.22	8424.39	8258.56	8085.21	7905.86
8	0.7093	144.1224	920.02	903.20	885.43	866.84	847.61
Ensemble PW molecular wt:			86.1	84.9	83.5	82.2	80.7
Calculation of sea water molecular weight				Mass Water / kg sw = 906.236g			
N-mer	Wt %	Mol Wt	Mass water × (%-nHB or %-HB) × wt % × mol wt				
1	100.0	18.0153	1632.59	1901.14	2185.08	2481.91	2789.02
2	0.1773	36.0306	52.11	51.16	50.15	49.10	48.01
3	3.2403	54.0459	1428.36	1402.25	1374.65	1345.80	1315.94
4	19.3629	72.0612	11380.37	11172.37	10952.45	10722.56	10484.70
5	39.9050	90.0765	29317.27	28781.45	28214.91	27622.68	27009.91
6	29.0443	108.0918	25605.82	25137.84	24643.02	24125.76	23590.57
7	7.5608	126.1071	7776.61	7634.49	7484.21	7327.11	7164.57
8	0.7093	144.1224	833.75	818.52	802.40	785.56	768.14
Solv H ₂ O + cations:		131.8489	9422.19	9422.19	9422.19	9422.19	9422.19
Ensemble SW molecular wt:			89.4	88.3	87.1	85.8	84.5

Table 1. Example calculation of the ensemble molecular weight for pure water and sea water ($S_p = 35$) as a function of temperature. N-mer weight-% is 100% for $n=1$ and a Gaussian distribution for $n=2-8$ (where $a=0.443012$, $b=90.0765$ and $c=18.0153$) times the n-mer molecular weight. The ensemble molecular weight is calculated as the sum of n-mer mass × molecular weight products divided by the sum of the n-mer masses (plus the cations in the case of sea water).